Hydrogen Bonding - The “Almighty” Weak Bond

Introduction

**Intermolecular forces** describe interactions *between* different molecules and play an important role in determining the physical properties of a substance. **Intramolecular forces** refer to interactions *within* a single molecule. The term intramolecular is often used to refer only to the relatively weak, non-chemical bonding interactions within a molecule that are often responsible for molecular conformation (*i.e.*, 3-D geometry) of compounds. Intramolecular interactions may also refer to the stronger covalent and polar bonding interactions within a molecule as well.

All substances exhibit some sort of intermolecular interactions. The type and strength of these interactions are determined by the nature of the atoms and bonds. The interactions may be described as ion-ion, ion-dipole, ion-induced dipole, dipole-dipole, dipole-induced dipole, or induced dipole-induced dipole or *dispersion*. You may have heard of dispersion before as London forces or van der Waals interactions. There is also a special, important type of interaction known as **hydrogen bonding**.

Hydrogen bonding (H-bonding) may occur both intra- and intermolecularly. Generally, hydrogen bonding involves a hydrogen atom bound to a highly electronegative atom, most commonly (but not exclusively!) oxygen, nitrogen, or fluorine. Due to the difference in electronphilicity between the hydrogen atom and the highly electronegative atom, call it “X,” a dipole is created in the H-X bond. That is, the hydrogen effectively carries a partial positive charge and the electronegative atom, X, carries a partial negative charge. (Here, “partial” implies that these charges are less than a full electron charge, *e.g.*, maybe $\pm 0.5e$ but not $\pm 1.0e$.) The partial positive charge on the hydrogen atom of the H-X bond can then lead to a reasonably strong interaction (as intermolecular interactions go) with another highly electronegative atom, call it “Y,” with a partial negative charge.

If this other highly electronegative atom is on a different molecule this X-H⋯Y interaction is an intermolecular hydrogen bond. If it is on the same molecule the X-H⋯Y interaction is an intramolecular hydrogen bond. In a crude way a hydrogen bond is analogous to a chemical bond: a chemical bond is formed when electrons between two nuclei attract them strongly enough to overcome the repulsion of their two positive charges whereas a hydrogen bond is formed when the positively charged hydrogen between two negatively charged atoms attracts those atoms strongly enough to overcome the repulsion of their two negative charges.

The notation for indicating a hydrogen bond is that shown above: X-H⋯Y. That is, the hydrogen bond itself is drawn as three or four dots, “…”, connecting the hydrogen to the electronegative atom Y. Hydrogen bonds tend toward linear geometries, that is X-H-Y angles close to 180°. However, they are typically not perfectly linear but have X-H-Y angles greater than about 140°. They are also marked by a relatively short X-Y distance, one that is longer than would be expected in an X-Y chemical bond, but shorter than would be expected based on the atomic radii of X and Y. The energy of a hydrogen bond is typically 15-40 kJ/mol. This can be compared to energy of a C-H chemical bond, roughly 400 kJ/mol, and the energy of dispersion (or van der Waals) interactions, roughly
1-5 kJ/mol.

Hydrogen bonding interactions can be particularly important in the condensed phase, that is, for liquids and solids. The presence or absence of hydrogen-bonding can have a profound impact on the physical properties of matter. For example, the properties of water, the most common liquid, can be explained by the presence of extensive network of hydrogen bonds. The function and structure of biological molecules relies critically on hydrogen bonding. Our genes are encoded in DNA molecules which are held together by hydrogen bonds and, more importantly, maintain the genetic code through specific hydrogen-bonding patterns. The structure and function of proteins in all biological organisms is governed in significant part by hydrogen bonds. Similarly, many synthetic materials, such as polymers (e.g., plastics), have properties that are determined by their hydrogen bonding interactions. The purpose of this experiment is to learn how intermolecular forces affect certain properties of substances.

By examining chemical structures along with the experimental data acquired in this lab experiment, you will begin to appreciate the significance of intermolecular and intramolecular interactions in chemical structure-property relationships. In Part 1 of this experiment, you will study the impact of intermolecular forces on energy changes that accompany the mixing of liquids. Disruption of an intermolecular interaction consumes energy, whereas the formation of an intermolecular interaction is accompanied by an energy release. When true mixing occurs, some intermolecular interactions are necessarily broken as new ones form. Thus, simple qualitative conclusions can be drawn from studies of the net temperature changes that occur when pairs of pure liquids are mixed in a systematic way. In the process of breaking and forming intermolecular interactions during mixing, the structures of the liquids may be changed in such a way that the volume of the solution is different than the sum of the volumes of the two components.

Intermolecular forces are also responsible for holding the molecules of solid materials in lattice positions. The temperature at which a solid substance is transformed to the liquid state is known as its melting point. Qualitatively, stronger intermolecular forces (or greater cohesive energy) are associated with substances that melt at higher temperatures. In Part 2, we will study the melting behavior of several different types of substances. You will investigate a series of nylon polymers that have similar composition but vary in the details of their structures. The differences in the structures of these polymers can result in significant changes in the melting points. In another experiment, you will determine the melting points of two other structurally similar substances, the isomeric acids fumaric acid and maleic acid, shown below. The hydrogen atoms shown in red are available to participate in hydrogen bonding.
Fumaric and maleic acids are called isomers because they share the same molecular formula but differ in the spatial positioning of their constituent atoms (a positioning that can only be changed by breaking a chemical bond). Consider the nature of the intermolecular forces responsible for holding molecules of these substances together in their respective solid phases. Do you expect the melting points of these pure substances to be similar or different?

The hydrogen atoms in red in the structures below are also responsible for the acid properties of the fumaric and maleic acids. By definition, an acid has a proton that can be chemically “donated” to a base. These protons can be lost through a reaction such as that below to produce $\text{H}^+$ (a positively charged hydrogen ion--simply a proton) in solution. Those acids that do not donate their protons very easily are termed weak acids; stronger acids donate their protons more readily. The acid strength (which describes the ease of removing $\text{H}^+$) is a property that may be affected by hydrogen bonding, acid strength, which describes the ease of removing $\text{H}^+$ from a molecule or ion. When discussing the acidity or basicity of a solution, pH is often invoked, where $\text{pH} = -\log[\text{H}^+]$. Acidic solutions have a $\text{pH} < 7$; basic solutions have a $\text{pH} > 7$. The differences in intermolecular interactions between these molecules can also result in different ability to undergo this reaction. The intermolecular interactions are therefore important not only for the physical properties of the molecules, but also for the chemical properties. Can you think of ways in which we could investigate acidity of the fumaric and maleic acid samples?

$$A - H \rightleftharpoons A^- + H^+$$

Pre-lab

**Safety:** Goggles must be worn at all times. Maleic acid and fumaric acid are irritating to the skin and should be rinsed off with water in the event of skin contact.

Some parts of the melting point apparatus become very hot to the touch, and could produce burns. Be careful not to touch the heating block or the metal parts that surround it when adding or removing melting point capillaries.

Organic solvent mixtures (water, isopropanol, acetone, and ethanol) should be collected in a separate container as waste. Used melting point capillaries should be handled by the top only to avoid burns, and must be discarded in the large glass waste container at the front of the room.
Read through this laboratory write-up in its entirety. Also read about intermolecular interactions in your text (e.g., sections 10.2 and 10.3 of *Principles of Modern Chemistry* by Oxtoby *et al.*).

**Pre-lab Assignment:** Please write out the following in your lab notebook. This assignment is due at the beginning of lab. You will not be allowed to start the experiment until this assignment has been completed and submitted to your TA.

- List the chemicals you will use for this week’s experiment. For each chemical, list specific safety precaution(s) that must be followed. To find specific safety information, obtain a Materials Safety Data Sheet (MSDS) on the chemical of interest. MSDSs can be found through an internet search (e.g., google) or from the following website: [www.hazard.com](http://www.hazard.com). Read the MSDS and find specific safety concerns for each chemical. Be sure to include the route(s) of entry and the possible acute and chronic effects of exposure, if given.

- Using your own words, complete the OBJECTIVE and PROCEDURE sections in your lab notebook. (See the [Maintaining Your Laboratory Notebook](#) link on the lab website to learn what these lab notebook sections entail.)

- Also, please write out answers to the questions below.

  1) *Briefly* describe the objectives of this experiment.
  2) Construct flow charts (one for Part 1, and one for Part 2) outlining the steps your group will follow to complete the experiment.
  3) Qualitatively, how would you predict the melting points of maleic and fumaric acid to vary based on their structures? Explain your answer.
  4) What types of intermolecular interactions are possible in the nylon samples?

In addition to these pre-lab requirements, a short quiz may be given at the beginning of lab based on the material in this lab write-up.

**Procedure**

**Part 1 - Temperature Changes upon Mixing Liquids**

Your TA will do a demonstration that involves volume changes in solutions upon mixing. Record your observations of this demonstration. Following this, you will determine the temperature change upon mixing for a variety of solvents. In this Part, you will systematically combine equal volumes of two liquids at a time to assess the temperature changes that accompany mixing. The following liquids are provided: distilled water, isopropanol, acetone, and ethanol.

1. Open the LoggerPro software and set it up to acquire temperature data with the Vernier temperature probe as described in the [online instructions](#).

2. Construct tables similar to the following table in your notebook containing the binary combinations of solvents you will test:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Isopropanol</th>
<th>Distilled Water</th>
<th>Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Use separate 10.0 mL-size graduated cylinders to obtain 2.00 mL each of distilled water and isopropanol. Pour the entire volume of distilled water into a small clean test tube.
4. Submerge the temperature probe in the isopropanol sample and record its initial temperature in your table. Submerge the temperature probe in the distilled water sample and record its initial temperature.

5. Remove the temperature probe from the water and carefully add the entire volume of isopropanol. Replace the temperature probe immediately, agitate gently, and record the “final” temperature. How will you know that the system has reached its final temperature? Compute the net temperature change as $\Delta T = T_{\text{final}} - T_{\text{initial}}$.

6. Repeat steps 2 through 5 for all other possible binary combinations of the four solvents. Make sure to dispose of the solvent mixtures in the appropriate waste container.

Discussion and Analysis: Identify the chemical structures of the solvents used in this experiment. What specific types of intermolecular forces would you expect to be present in each substance prior to mixing? What new forces are present after each particular solvent pair is mixed? Based on these considerations, propose explanations for each of the temperature changes that your group observed.

Part 2 - Melting Points

In this Part, you will determine the melting points for four different nylon samples as well as two powders: fumaric acid and maleic acid (whose structures were given above). Each sample will be placed in a transparent glass “capillary tube” so that it can be gradually heated and observed using a melting point apparatus. The nylon samples selected have either differences in the arrangement of the functional groups or the length of the alkyl chains connecting the functional groups. The structures of the compounds are listed below:

**Nylon 6 (PA 6)**
Repeat Unit: [---NH(CH₂)₅CO---]ₙ

**Nylon 12 (PA 12)**
Repeat Unit: [---NH(CH₂)₁₁CO---]ₙ

**Nylon 6/6 (PA 66)**
Repeat Unit: [---NH(CH₂)₆NHCO(CH₂)₄CO---]ₙ

**Nylon 6/10 (PA 610)**
Repeat Unit: [---NH---(CH₂)₆---NHCO---(CH₂)₆CO---]ₙ

For information about the synthesis of these polymers as well as additional information about the structures, see [http://en.wikipedia.org/wiki/Nylon](http://en.wikipedia.org/wiki/Nylon). These polymers are of commercial importance and therefore information about their properties, synthesis, and uses is readily available by searching online. Additional samples of other nylon samples may be available for analysis if time permits.

1. Use a small spatula or scoopula to obtain small samples (smaller than the size of a pea) of the sample of interest. (For the nylon samples, you will use small slivers of the sample.) Be sure to keep track of the sample identities!

2. Obtain a melting point capillary. Place one of the samples in the open end of the capillary. You may have to invert the capillary and scoop up the sample; tap or bounce the capillary gently on the bench to force the sample to the bottom. A small sample loaded into a 2 to 4 mm length at the bottom of the capillary will work best.

3. The melting point apparatus bears a conventional thermometer that should not be removed at any time. Read this thermometer to confirm that the heating block of the apparatus has cooled to 100°C or less. If the temperature exceeds 100°C, locate the power switch and confirm that it is off, and wait until the temperature drops to 100°C or less before continuing.
4. **Be careful not to touch the heated regions of the melting point apparatus.** Place the loaded melting point capillary into a sample holder. The sample holders are the small “capillary-sized” vertical channels to the right of the thermometer base.

5. Adjust the heating intensity knob to a setting of 5 and turn on the power switch. Ensure that the solid sample is visible through the magnifying lens.

6. Watch the sample carefully through the lens. When the sample begins to melt, its solid structure will begin to collapse, much like the melting of ice shavings on a warm day. When this process begins, note the temperature immediately, but quickly resume observation of the sample. When the sample has completely melted, note the temperature once again. Usually, the starting and ending temperatures are not identical; as such, it is important to record this *melting range* in lieu of a discrete melting point.

7. Turn off the melting point apparatus power switch.

8. Carefully remove the hot capillary, handling it by the top only to prevent burns, and place it in the glass waste container.

9. Repeat steps 2 through 8 for each of the nylon samples as well as the fumaric and maleic acid. Ensure that the temperature has cooled well below the melting point of the next sample before placing the loaded capillary into the melting point apparatus. The heat setting may need to be adjusted for different samples, depending on the melting point for a particular sample. A setting of 7 or higher is recommended for fumaric acid.

10. **Follow your TA’s instructions concerning pooling data and making replicate measurements.**

   If time permits, you should also investigate the acidity of the fumaric and maleic acid samples. The pH probe can be used to determine the pH of an aqueous solution of each of these acid samples. Your TA can help you with this measurement. Are the pH values different for these two samples? Use your understanding of the interactions of these molecules to explain your results.

**Discussion and Analysis:** Based on an examination of the chemical structures of the two weak acids studied, what types of intermolecular and intramolecular forces are present in these solid materials? What types of interactions are present within the nylon samples? Based on the structures or the different nylon samples, what differences would you expect in the strength of the interactions? Considering the differences in the nature of these forces, can you rationalize a difference in the melting points? How does the prediction based on the molecular structures compare to your actual experimental observations? Discuss the difference(s) between the multiple measurements of the melting point and its implication for the reliability of your conclusions.

**Report**

Your lab report should be a formal, individual report prepared according to the “Guidelines for Laboratory Reports” you have been given. In addition to the categories discussed in these guidelines you should provide answers to all the questions posed in this laboratory experiment write-up.

**References**


http://invention.smithsonian.org/centerpieces/whole_cloth/u7sf/u7images/act1/nd13.jpg
http://commons.wikimedia.org/wiki/Image:PA6-PA66.png